

NASA Technical Paper 1407

Three Methods for In Situ  
Cross-Linking of Polyvinyl  
Alcohol Films for Application  
as Ion-Conducting Membranes in  
Potassium Hydroxide Electrolyte

**DISTRIBUTION STATEMENT A**

Approved for public release;  
Distribution Unlimited

Warren H. Philipp and Li-Chen Hsu

APRIL 1979

19960223 127

DTIC QUALITY INSPECTED 8

**NASA**

DEPARTMENT OF DEFENSE  
PLASTICS TECHNICAL EVALUATION CENTER  
ARRADCOM, DOVER, N. J. 07801

PLASTEC 31715

NASA Technical Paper 1407

Three Methods for In Situ  
Cross-Linking of Polyvinyl  
Alcohol Films for Application  
as Ion-Conducting Membranes in  
Potassium Hydroxide Electrolyte

Warren H. Philipp and Li-Chen Hsu  
*Lewis Research Center*  
*Cleveland, Ohio*



National Aeronautics  
and Space Administration

**Scientific and Technical  
Information Office**

1979

## SUMMARY

Three methods for in situ cross-linking of water soluble polyvinyl alcohol films are presented. These cross-linked films show promise for use as battery separators in aqueous potassium hydroxide (KOH) electrolyte. Electrical resistivities in KOH of cross-linked membranes representing the three procedures are given with a brief discussion of the chemical mechanism involved in their preparation. Physical properties, such as mechanical strength and swelling in alkaline electrolyte, are discussed.

The three cross-linking techniques entail:

(1) Treating a polyvinyl alcohol membrane containing a specified amount of a dialdehyde such as glutaraldehyde with an acid solution which catalyzes acetalization cross-linking.

(2) Treating a polyvinyl alcohol film with periodic acid which cleaves the few 1,2 diol units present in polyvinyl alcohol with the formation of aldehyde groups which then causes cross-linking via acetalation of the 1,3 diol units.

(3) Reacting a polyvinyl alcohol film with hydrogen atoms and hydroxyl radicals from irradiated water whereby cross-linking is accomplished by polymer radicals formed as a consequence of hydrogen abstraction. Hydrogen abstraction cross-linking of films containing both polyvinyl alcohol and polyacrylic acid in polymer solution improves strength in 45 percent KOH. Films made from solely polyacrylic acid were unsatisfactory.

All three methods have merit. The first method affords best control over the extent of cross-linking. The second treatment with periodic acid provides greatest oxidation resistance to the cross-linked film because the easily cleaved 1,2 diol units are eliminated. The third process involving radiation can provide films of very high ionic conductivity in KOH electrolyte.

## INTRODUCTION

The coulombic and energy efficiency, cycle life, and power output of alkaline batteries are dependent upon effective low-resistance battery separators. Thus a substantial amount of battery research is concerned with development of better battery separators. Separators have been fabricated from films or membranes composed of hydrophilic organic polymers that include polyvinyl alcohol, polyethylene grafted with acrylic acid, and copolymers with active carboxylic groups. The regenerated cellulose film

was one of the earliest practical battery separators for Ag-Zn and Ni-Zn alkaline batteries, but the highly oxidative environment in Ag-Zn cells eventually deteriorated such separators. These separators were replaced by more effective and oxidation stable inorganic-organic separators (refs. 1, 2, and 3). Cellulose separators are still being used in some alkaline Ni-Zn cells for which oxidation of the separator is less severe.

This investigation is directed toward new polymeric systems that we anticipate will lead to the development of improved low cost separators for alkaline batteries. The previous paper (ref. 4) describes the preparation of a two-component, single-phase film cast from water solution. The dried film can easily be fabricated into electrode bags. Treatment of the film with an aqueous formaldehyde solution containing a small amount of a mineral acid converts one of the film components, polyvinyl alcohol, to insoluble polyvinyl formal. The newly formed polyvinyl formal component serves as the structural matrix for the film. The second and hydrophylic film component, polyacrylic acid, permits ion transport in KOH electrolyte. One objection to such a film is that the polyacrylic acid might eventually be leached out. To overcome this objection, our subsequent work has been directed toward making hydrophylic groups a chemical part of the matrix.

Three methods for making such films are presented in this report. All three processes involve in situ cross-linking of polyvinyl alcohol films which makes them insoluble in aqueous systems. The chemical reactions involved in the methods are summarized in the Encyclopedia of Polymer Science and Technology (ref. 5). The third technique is useful for cross-linking films comprising polyvinyl alcohol - polyacrylic acid polymer blends. The three methods are:

1. Cross-linking by acetalization of the 1, 3 diol units of polyvinyl alcohol with a dialdehyde such as glutaraldehyde.
2. Cross-linking by acetalization with aldehyde formed via in situ selective oxidative cleavage with periodic acid of the 1, 2 diol units, a minor constituent in polyvinyl alcohol. This results in chain cleavage and extension as well as cross-linking.
3. Cross-linking of polyvinyl alcohol or polyvinyl alcohol - polyacrylic acid films via hydrogen abstraction by reaction of the polymeric material with the radicals from irradiated water, namely hydrogen atoms and hydroxyl radicals.

An advantage of in situ cross-linking is the ease of fabricating articles such as films, electrode bags, and impregnated support matrices from an aqueous solution of the water soluble linear polymer. The finished article can then be made water insoluble by a simple cross-linking treatment. Aqueous systems are employed in all cases thereby giving the additional advantage of avoiding the use of objectionable organic solvents. Moreover the base polymers, polyvinyl alcohol and polyacrylic acid are commercially available and relatively inexpensive.

## EXPERIMENTAL

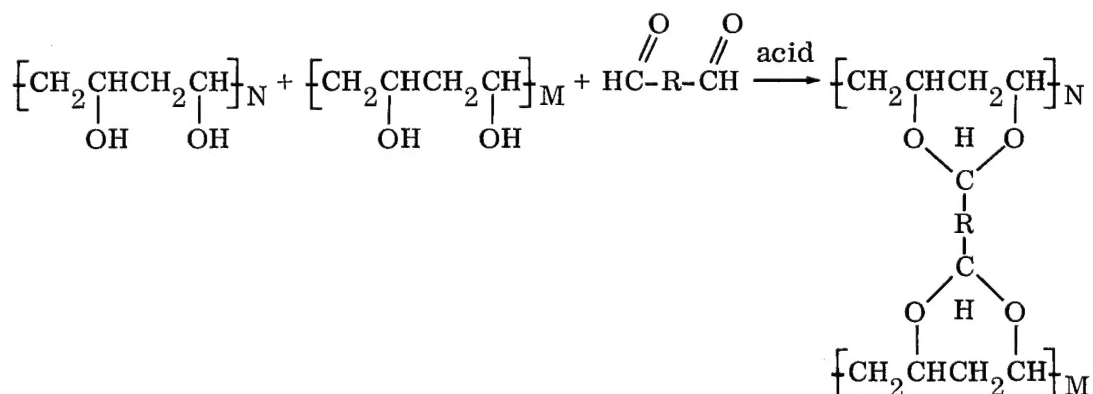
## Starting Materials and Film Casting

Both high molecular weight (M.W.) and low molecular weight polyvinyl alcohol were obtained from Polysciences, Inc. (for 4% in water: high M.W. visc. 55 to 65 cP and low M.W. visc. 4 to 6 cP). Stock solutions of the following concentrations were used: 10 percent aqueous high M.W. and 20 percent low M.W. Above these concentrations the viscosity was too high to afford convenient handling. Aqueous polyacrylic acid was made by the standard method of polymerizing the corresponding monomer by means of a potassium persulfate catalyst. Glutaraldehyde was obtained as a 50-percent aqueous solution from Eastman Kodak. Casting solutions were made by mixing the various solutions in the desired proportions. To prevent premature cross-linking with glutaraldehyde, a few drops of concentrated aqueous ammonia were added.

Polymer films containing polyvinyl alcohol with or without other materials were made by casting on smooth glass with a Gardner knife the appropriate aqueous solution of the polymeric material. After evaporation of the water at room temperature, the film was easily removed from the glass. The dried film was then cut into 11- by 7-cm sheets that were then cross-linked by subsequent treatments.

### Method I - Cross-linking with Added Organic Dialdehyde

Polyvinyl alcohol reacts with aldehydes in acid media to form water insoluble polyacetals (ref. 6). Reaction with dialdehydes is expected to form an acetal cross-linked structure as indicated by the equation



Acetalization of polyvinyl alcohol films has been accomplished by simply immersing the film in a hot aqueous solution of the aldehyde containing a small amount of mineral acid, usually sulfuric acid,  $\text{H}_2\text{SO}_4$  (ref. 4). A salting out agent such as sodium sulfate,

$\text{Na}_2\text{SO}_4$ , was added to decrease solubility of the polymer during the acetalization reaction. The extent of acetalization by this procedure was difficult to control and usually went too far, producing films of poor ionic conductivity in alkaline electrolyte. The poor conductivity is attributed in part to the low density of hydrophylic OH groups remaining in a highly acetalated film.

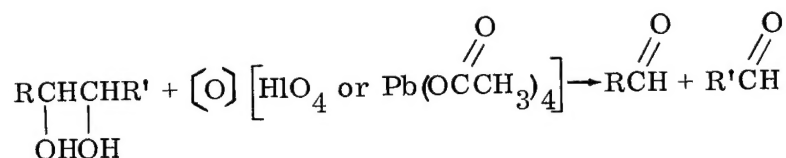
Better control of acetalization should be obtained by adding a specified amount of the mono or dialdehyde directly to the aqueous polyvinyl alcohol casting solution; the aldehyde, if its vapor pressure is not too high, remains incorporated in the polymer after drying. Glutaraldehyde served as a suitable dialdehyde for our cross-linking purpose. Air dried polyvinyl alcohol films about 150 to 180 micrometers thick, containing  $2\frac{1}{2}$ , 5, 10, and 20 percent glutaraldehyde were treated with the following solution at  $70^\circ\text{C}$  for 1 hour. The solution contained 1 liter water, 20 ml concentrated  $\text{H}_2\text{SO}_4$ , and 200 grams  $\text{Na}_2\text{SO}_4$ .

The sulfuric acid catalyzes the acetalization, and the sodium sulfate inhibits the solubility of the polyvinyl alcohol film. The treated film was washed with water and treated with 1 percent aqueous HCl at  $70^\circ\text{C}$  for  $1/2$  hour to complete the reaction. At this time the film has lost its water solubility; subsequent salting out was unnecessary. After the HCl treatment, the film was immersed for several minutes in water and then in dilute sodium bicarbonate solution to neutralize acid residues. This is an important step if dried films are to be stored for long time periods because acid remaining in the film causes decomposition of the acetalized polymer (ref. 6). The film was again immersed in water several times to remove salts and then air dried at room temperature. The dried tough film was cut into 4- by 4-cm test specimens and stored in 45 percent KOH for at least 24 hours prior to the taking of resistivity measurements.

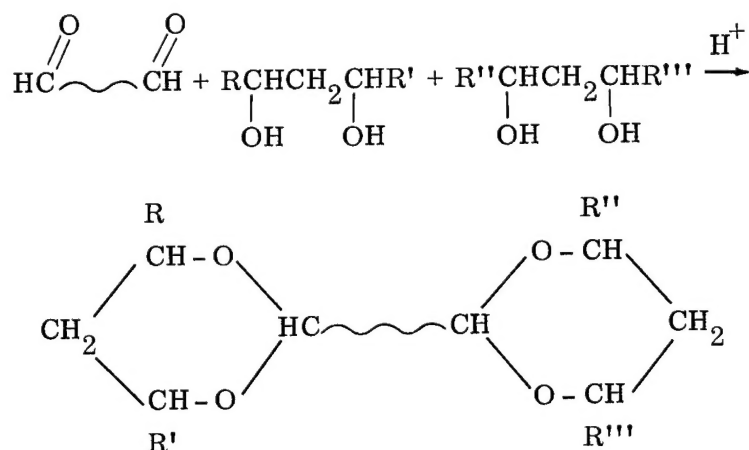
## Method II - Cross-linking by Acetalization Via Selective Oxidative

### Cleavage of the 1,2 Diol Units

Polyvinyl alcohol is essentially a 1,3 diol polymer; however, the commercial material contains about 1 to 2 mole percent 1,2 diol units in the molecular structure. Certain oxidizing agents involving divalent reduction such as periodic acid (ref. 7, p. 368) and lead (IV) acetate (ref. 7, p. 398) oxidatively cleave such 1,2 diol units with the specific formation of aldehyde end groups. Under certain conditions (e.g., low temperature), ceric salts cause gelation of aqueous polyvinyl alcohol solution by a similar mechanism (refs. 8 and 9). The cleavage reaction is represented by the following equation:



Aldehydes in acid media undergo acetalization with 1, 3 diols as exemplified in Method I. Following the cleavage of the 1, 2 diol units, the resultant aldehyde end groups acetalate the 1, 3 diol units of the polyvinyl alcohol resulting in reformed polymer chains and cross-linking. This may be illustrated as follows:



The cleavage and acetalization can be accomplished in a single in situ treatment of the polyvinyl alcohol film or fabricated electrode bag. This was achieved by immersing the film for a specified time in a hot acid solution of potassium periodate. A typical procedure was to expose the polyvinyl alcohol film or bag in the following periodate solution at 70° C for about an hour. The solution contained 1 liter water, 30 grams  $\text{KIO}_4$ , 50 ml concentrated  $\text{H}_2\text{SO}_4$ , and 200 grams  $\text{Na}_2\text{SO}_4$ .

As mentioned previously, the sodium sulfate serves to salt out the polyvinyl alcohol. After treatment the film was washed with water, then with dilute aqueous sodium bicarbonate to neutralize residual acid and finally with water. The film was air dried at room temperature. As was the case with the glutaraldehyde treated polyvinyl alcohol film, the dried periodate treated film is tough and resists tearing.

Tetravalent lead salts should accomplish the same result; however, their use is inconvenient because organic solvents are required. Generally lead (IV) acetate is dissolved in glacial acetic acid; lead (IV) acetate hydrolyzes in aqueous media to precipitate lead (IV) oxide.



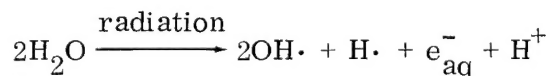
### Method III - Cross linking of Films Via Hydrogen Abstraction

Previous investigations (ref. 10) have demonstrated that exposure of certain aqueous polymer solutions to ionizing radiation causes gelation because of cross-linking. Water soluble polymers that radiatively cross-link in aqueous solution are polyvinyl alcohol, polyvinyl pyrrolidone, and polyacrylic acid. The radiolytic cross-linking of polyvinyl alcohol solutions by Cobalt-60 gamma source has been studied by Danno (ref. 11). He observed that gamma irradiation of aqueous polyvinyl alcohol at first resulted in gelation; on further irradiation the gel shrank with the separation of water to form a crust of cross-linked polymer. The cross-linked polymer thus formed did not dissolve even when autoclaved with water at 150° C for 1 hour and retained its original shape when boiled in either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide for 3 hours. Henglein (ref. 12) suggested that cross-linking in aqueous solution involves hydrogen abstraction from the radicals in irradiated water.

Our method makes use of high energy electrons, 2 MeV from a linear accelerator (Dynamitron) for the in situ cross-linking of polyvinyl alcohol, and high M.W. polyvinyl alcohol-polyacrylic acid polymer blend films and electrode bags. As an example, we used a polymer blend comprising a 2-to-1 weight ratio polyvinyl alcohol to polyacrylic acid. Because of the considerably higher radiation flux capacity of the dynamitron compared with that available from a Cobalt-60 source, extensive cross-linking could be accomplished in a much shorter time.

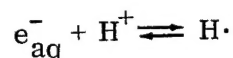
The dried films or electrode bags, prior to irradiation, were soaked for several hours in a solution consisting of 1 liter water, 20 ml concentrated H<sub>2</sub>SO<sub>4</sub>, and 200 grams Na<sub>2</sub>SO<sub>4</sub>. The wetted film was placed in a round glass crystallizing dish 19 cm in diameter, 10 cm deep and covered with 100 ml of the aforementioned solution. The submerged film was then irradiated for a specified time with 2 MeV electrons at a beam current density of 10<sup>-7</sup> A-cm<sup>-2</sup>. The irradiation time ranged from 5 to 20 minutes. The irradiated polyvinyl alcohol films were washed with water, then with dilute sodium bicarbonate solution, and finally with water. The film was then air dried at room temperature. To prevent tearing, care was taken in handling wet cross-linked films containing polyacrylic acid. No treatment with sodium bicarbonate solution was used on these films because the films swollen by the formation of sodium polyacrylate were particularly weak. The films did not swell too much when placed in 45 percent KOH because of the salting out effect of the high solute concentration.

The radicals formed when water is exposed to ionizing radiation are hydroxyl radicals (OH•), hydrogen atoms (H•), and hydrated electrons (e<sub>aq</sub><sup>-</sup>); that is,

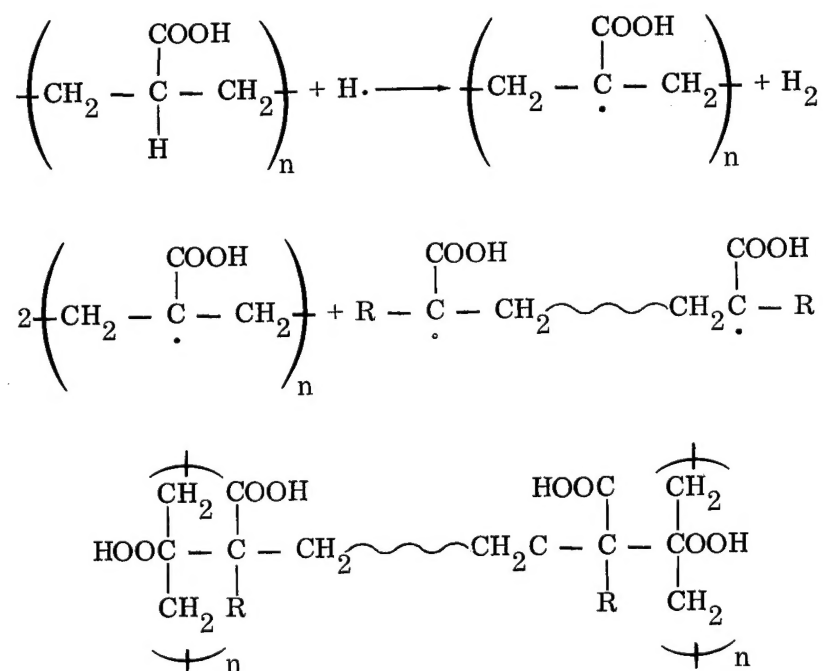




In acid media,  $e_{aq}^-$  is converted to  $H\cdot$  according to the equation



Because hydrogen atoms are effective in hydrogen abstraction cross-linking, the films were irradiated in acid solution which favors the formation of hydrogen atoms over the production of hydrated electrons. The cross-linking mechanism is believed to involve the abstraction of hydrogen atoms on the alpha carbon of the polymer. The resulting linear polymer radicals then cross-link at the alpha carbon as indicated by the following equation for polyacrylic acid:



A similar cross-linking mechanism may also apply to polyvinyl alcohol. The structure of the irradiated polyvinyl alcohol-polyacrylic acid blend is uncertain; however, the structure falls into one of two categories, namely, a cross-linked copolymer of the two polymers or simply a two-component system of cross-linked polyacrylic acid in a cross-linked polyvinyl alcohol matrix.

### Resistivity Measurements

The dc resistance measurements in KOH electrolyte were made according to the procedure given in the Air Force Laboratory publication on screening methods for battery separators (ref. 13). Each value of resistivity given in the tables is an average

from three film samples. In most cases, resistivity data gave a maximum spread of about 25 percent from this average. It is not the purpose of this report to provide exact resistivity data, but to show the relative value for each cross-linking technique.

Film thickness was measured with a micrometer. Physical properties such as mechanical strength and degree of swelling were only noted qualitatively.

## RESULTS AND DISCUSSION

### Method I

Resistivity data for glutaraldehyde cross-linked polyvinyl alcohol films are shown in table I. As expected, the resistivity increases with increasing glutaraldehyde content in the film. Films containing 20 percent glutaraldehyde, the highest concentration reported, are essentially nonconducting. Cross-linking appears to be extensive at this concentration as indicated by the hard somewhat brittle nature of these films whereas films containing lower concentrations of glutaraldehyde (e.g.,  $2\frac{1}{2}$  percent) are significantly more flexible. The poor conductivity of the highly cross-linked films is probably due to the poor electrolyte absorption in the membrane that arises not only from the rigidity of the cross-linked structure but also from the decreased OH group concentration as a consequence of extensive acetalization. Sufficient cross-linking was obtained at our lowest glutaraldehyde concentration of  $2\frac{1}{2}$  percent to give tough and water insoluble films with little swelling when the membrane was immersed in aqueous KOH. We anticipate that membranes containing less than  $2\frac{1}{2}$  percent glutaraldehyde would also give tough water insoluble films of good conductivity in 45 percent KOH.

For in situ cross-linking of polyvinyl alcohol films, the main advantage of incorporating the dialdehyde in the film itself rather than in an acetalizing reagent is better control over the extent of cross-linking. In this case the amount of cross-linking is limited by the amount of dialdehyde in the film. Attempts to control the extent of acetalization using time, temperature, and dialdehyde concentration in the reagent solution have not been too successful. Results of such exploratory experiments (ref. 4) show inconsistent film resistivities in 45 percent KOH. It is especially difficult to maintain good reproducibility at low cross-linking levels using time, temperature, and concentration methods; and it is the low level cross-linked films that are of greatest interest for alkaline battery separators.

To illustrate Method I we selected glutaraldehyde because it is readily available, forms a homogeneous film with polyvinyl alcohol, and has a low enough vapor pressure so as to remain in the film after drying. No doubt other dialdehydes or even polyaldehydes with similar properties could be used. A modification of this cross-linking tech-

nique would be the use of dialdehydes or polyaldehydes containing hydrophylic groups such as hydroxyl or carboxylic acids.

### Method II

The second in situ cross-linking technique involved the treatment of polyvinyl alcohol films with periodic acid. Treated films were tough, and resisted tearing; practically no swelling was observed after a 24-hour exposure to 45 percent aqueous KOH. A comparison of resistivities for treated versus untreated films given in table II shows an almost threefold resistivity increase for the cross-linked films. This indicates a higher degree of cross-linking than is desired for good ionic conduction. However, because of the high strength of periodate treated membranes, one should be able to design around this high resistance by fabricating thinner membranes.

The degree of cross-linking in periodic acid treated films is dependent on the proportion of 1,2 diol units in the 1,3 diol structure of polyvinyl alcohol. This proportion is related to the proportion of head-to-head units to head-to-tail units in the original starting material, polyvinyl acetate from which polyvinyl alcohol is made by hydrolysis. Head-to-head units in polyvinyl acetate of course lead to the 1,2 diol units. The commercial material used in our study contains about 1 to 2 percent of 1,2 diol units. Low temperature polymerization of vinyl acetate reduces head-to-head polymerization.

### Method III

The third cross-linking techniques for polyvinyl alcohol and polyvinyl alcohol - polyacrylic acid polymer blend films is based on the reaction of these materials with the radicals in irradiated water. These cross-linked films have low resistivity in 45 percent KOH; see tables III, IV, and V. The resistivities of the cross-linked films comprising a 2-to-1 weight ratio polyvinyl alcohol - polyacrylic acid are the lowest in resistivity of all the films tested.

The resistivities in 45 percent KOH of films composed of just polyvinyl alcohol exposed to 2 MeV electrons (table III) appear to be practically independent of radiation time; the values are about 33 ohm-cm and 21 ohm-cm for the high molecular weight and low molecular weight polyvinyl alcohol, respectively. Variations in area resistivities (ohm-cm<sup>2</sup>) are attributed to differences in film thickness and possible film defects (e.g., small bubbles and cracks) formed during processing. The consistent low resistivities at increasing radiation dose implies that hydrophylic OH groups are not significantly lost during cross-linking; thus, it would appear that cross-linking does not involve the OH functional group per se. There is one apparent anomaly to the indepen-

dence of resistivity with radiation dose; the average resistivity of unirradiated high molecular weight polyvinyl alcohol (52 ohm-cm) appears to be somewhat higher than the average value for irradiated films (33 ohm-cm).

The irradiated polyvinyl alcohol films have good mechanical properties and manifest only slight swelling in 45 percent KOH. However, in time the irradiated films immersed in 45 percent KOH develop an amber coloration; this discoloration forms at an accelerated rate in hot (100° C) 45 percent KOH. The intensity of the amber color is a function of radiation dose; highly irradiated films turn almost black with 12 hours when immersed in 45 percent KOH at 100° C. No dependence of color intensity on resistivity has been observed.

The coloration is not removed by hypochlorite or permanganate oxidation rather, it is bleached by strong reducing agents such as sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) and sodium borohydride. Bleaching of the amber coloration was conveniently achieved by treating the discolored films with hot aqueous alkaline sodium dithionite. Typically, irradiated polyvinyl alcohol films were discolored by exposing them to 45 percent KOH at 100° C overnight. Bleaching was accomplished by immersing the colored films at 90° C in a solution consisting of 1 liter water, 100 grams  $\text{Na}_2\text{S}_2\text{O}_4$ , and 50 grams NaOH. After about 5 hours the amber coloration practically disappeared. In the case of strongly colored films characteristic of highly irradiated films a slightly yellow color still persisted even after a 10-hour treatment. On reexposure of the bleached films to hot 45 percent KOH, the amber color was observed to develop again but to a lesser extent than in the unbleached films. The reduced films have good mechanical properties and, as shown in table IV, the resistivities are less than those for the irradiated films alone; it is probably due to the interaction of additional functional groups.

With the idea of achieving films of extremely low resistivity in KOH electrolyte, membranes containing the highly hydrophilic carboxylic acid group were made by irradiating membranes containing polyacrylic acid by the same radiation technique as was used for the polyvinyl alcohol films. As expected, the presence of polyacrylic acid in the films did improve conductivity of irradiated membranes as shown in table V for a polyvinyl alcohol-polyacrylic acid weight ratio of 2-to-1. These cross-linked films swelled considerably in 45 percent KOH; thus the mechanical properties of the cross-linked blend film were inferior to those cross-linked films containing just polyvinyl alcohol. For practical use in battery separators, the various parameters such as film thickness, radiation dose, and especially the ratio of polyvinyl alcohol to polyacrylic acid in the polymer blend film should be investigated further. A compromise between low resistivity and good mechanical properties should involve decreasing the proportion of polyacrylic acid in the membrane.

We have shown that, when an aqueous solution of polyacrylic acid is irradiated with high energy electrons, a water insoluble polymer crust forms which is indicative of

cross-linking. Irradiation of polyacrylic acid films in the same manner as described in this report rendered them water insoluble but the accompanying high degree of swelling resulted in poor mechanical strength. In 45 percent KOH that neutralizes the polyacid and converts it to its potassium salt, the poor mechanical properties were amplified. In 45 percent KOH, the films swelled to a soft gelatinous mass which was too weak to allow reliable resistivity measurements to be made.

The chemical structure of the irradiated polymer blend is in question as to whether it is simply a solution of cross-linked polyacrylic acid in a cross-linked polyvinyl alcohol matrix or actually a one-component copolymer system.

### CONCLUSIONS

This investigation has shown that all three in situ cross-linking methods may be applicable to battery separator technology. Each method has its own merits. The first process in which the cross-linking agent, a dialdehyde, is incorporated into the polyvinyl alcohol film affords good control over the extent of cross-linking. The higher the proportion of dialdehyde to polymer in the film, the greater the extent of cross-linking. For battery separators, a low degree of cross-linking is better than extensive cross-linking in terms of ionic conductivity. The extent of cross-linking should be minimized for best ionic conductivity (lowest resistivity) but should be sufficient to insure good mechanical properties. Other dialdehydes as well as those with more than two aldehyde groups may conceivably be incorporated into polyvinyl alcohol films to give a variety of cross-linked structures. The selection of cross-linking aldehydes is limited to those that are miscible with the polyvinyl alcohol casting solution as well as with the dry polymer film.

The second cross-linking method utilizing periodic acid is designed to provide greater oxidation resistance to the cross-linked film because the easily oxidatively cleaved 1,2 diol units are essentially used up in the reaction. In linear polyvinyl alcohol, the 1,2 diol units in the inherently 1,3 diol structure represent a chemically weak point for the oxidative cleavage in the polymer chain. Cleavage in the linear polyvinyl alcohol backbone results in physical deterioration of film integrity. Controlling the extent of cross-linking is less convenient in this case than it is for the first method because it depends on the number of head-to-head units in the polyvinyl acetate starting material. Although the periodic acid treated polyvinyl alcohol films had excellent mechanical properties, their resistivities were higher than films treated by the other two methods.

Our third cross-linking mode, based on the reaction of polyvinyl alcohol, and polyacrylic acid with the radicals of irradiated water is the most versatile of the three

methods because the other two are restricted to polyvinyl alcohol films. Irradiation of water soluble polyacrylic films made them water insoluble; however, when these films were immersed in 45 percent KOH they swelled to such an extent that their physical strength was poor. Significantly stronger cross-linked films were obtained when polyacrylic acid was incorporated with polyvinyl alcohol to form a polymer blend. The irradiated film comprising a 2-to-1 polyvinyl alcohol - polyacrylic acid polymer blend had the lowest resistivity in 45 percent KOH of all the cross-linked films presented in this report. A better compromise between high mechanical strength and low resistivity may be accomplished by decreasing the polyacrylic acid content of the films.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, December 15, 1978,  
506-16.

#### REFERENCES

1. Arrance, Frank C.; and Rosa, Albert G.: Flexible Matrix and Battery Separator Embodying It. U.S. Patent 3,625,770, Dec. 1971.
2. Bozek, John M.: Structure and Function of an Inorganic-Organic Separator for Electrochemical Cells - Preliminary Study. NASA TM X-3080, 1974.
3. Phillip, Warren H.; and May, Charles E.: Functioning of Inorganic/Organic Battery Separators in Silver-Zinc Cells. NASA TM X-3357, 1976.
4. Phillip, Warren H.: Polymeric Membrane Systems of Potential Use for Battery Separators. NASA TM X-3567, 1977.
5. Encyclopedia of Polymer Science and Technology. Vol. 14, Section V, Vinyl Alcohol Polymers. N. M. Bikales, exec. ed., John Wiley & Sons, Inc., 1971, pp. 149-239.
6. Sorenson, Wayne R.; and Campbell, Tod W.: Preparative Methods in Polymer Chemistry. Interscience Publisher, 1961, p. 176.
7. Bunton, C. A.: Glycol Cleavage and Related Reactions. Oxidation in Organic Chemistry, Part A, Vol. 5, K. B. Wiberg, ed., Academic Press, Inc., 1965, Chapt. VI.
8. Ikada, Yoshito: Reaction of Polyvinol Alcohol with Tetravalent Ceric Ion. J. Polymer Sci.: PC, vol. 15, no. 2, 1977, pp. 451-460.
9. Mino, G.; Kaizerman, S.; and Rasmussen, E.: The Oxidation of Polyvinyl Alcohol by Ceric Ion. J. Polymer Sci., vol. 39, 1959, pp. 523-529.

10. Alexander, P.; and Charlesby, A.: Effect of Radiation on Synthetic Polymers. J. Polymer Sci., vol. 23, 1957, pp. 355-376.
11. Danno, Akibumi: Gel Formation of Aqueous Solution of Polyvinyl Alcohol Irradiated by Gamma Rays from Cobalt-60. J. Phys. Soc. Jpn., vol. 13, no. 7, July 1958, pp. 722-727.
12. Henglein, Arnim: Crosslinking of Polymers in Solution Under the Influence of  $\gamma$ -Radiation. J. Phys. Chem., vol. 63, Nov. 1959, pp. 1852-1858.
13. Cooper, J. E.; and Fleischer, Arthur, eds.: Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries; Screening Methods. Air Force Systems Command, Aero Propulsion Lab., 1964.

TABLE I. - RESISTIVITY OF GLUTARALDEHYDE CROSS-  
LINKED POLYVINYL ALCOHOL FILMS IN  
45 PERCENT AQUEOUS KOH

Polymer	Glutaraldehyde, percent	Film thickness, $\mu\text{m}$	Area resistivity, $\text{ohm-cm}^2$
High M.W. PVA <sup>a</sup>	20	170	100
	10	160	2.72
	5	160	.89
	2.5	160	.49
	0	150	.37
Low M.W. PVA <sup>b</sup>	10	170	1.33
	2.5	170	.46
	0	160	.47

<sup>a</sup>Viscosity 55 to 65 cP for 4% in water.

<sup>b</sup>Viscosity 4 to 6 cP for 4% in water.



TABLE II. - RESISTIVITY IN 45 PERCENT AQUEOUS KOH OF  
PERIODATE TREATED VERSUS UNTREATED  
POLYVINYL ALCOHOL

Polymer	Untreated		Periodate treated	
	Thickness, $\mu\text{m}$	Area resistivity, $\text{ohm-cm}^2$	Thickness, $\mu\text{m}$	Area resistivity, $\text{ohm-cm}^2$
High M.W. PVA	150	0.37	200	1.02
Low M.W. PVA	160	.47	180	1.37

TABLE III. - RESISTIVITY IN 45 PERCENT AQUEOUS KOH OF RADIATION  
CROSS-LINKED POLYVINYL ALCOHOL MEMBRANES

Polymer	Thickness, $\mu\text{m}$	Beam flux, $\text{A-cm}^{-2}$	Radiation time, min	Area resistivity, $\text{ohm-cm}^2$	Resistivity, $\text{ohm-cm}$
High M.W. PVA	120	0	0	0.58	48
	180	0	0	.97	54
	160	$10^{-7}$	5	.59	37
	260	↓	5	.82	32
	260		10	.76	30
	180		30	.57	32
Low M.W. PVA	225	0	0	0.50	22
	250	$10.7$	5	.49	20
	290	↓	12	.65	22
	215		25	.36	16
	270		60	.70	26

TABLE IV. - COMPARISON OF RESISTIVITY IN 45 PERCENT AQUEOUS KOH OF REDUCED VERSUS  
UNREDUCED CROSS-LINKED POLYVINYL ALCOHOL FILMS

Polymer	Beam flux, $\text{A-cm}^{-2}$	Radiation time, min	Thickness, $\mu\text{m}$	Untreated		Reduced	
				Area resistivity, $\text{ohm-cm}^2$	Resistivity, $\text{ohm-cm}$	Area resistivity, $\text{ohm-cm}^2$	Resistivity, $\text{ohm-cm}$
High M.W. PVA	$10^{-7}$ ↓	30	150	0.46	31	0.16	11
		30	180	.57	32	.32	18
Low M.W. PVA		30	215	.68	32	.35	16
		60	270	.70	26	.45	17

TABLE V. - RESISTIVITY IN 45 PERCENT AQUEOUS KOH  
OF RADIATION CROSS-LINKED FILMS COMPRISING  
HIGH M.W. POLYVINYL ALCOHOL:  
POLYACRYLIC ACID IN A 2-TO-1 WT. RATIO

Thickness, $\mu\text{m}$	Beam flux, $\text{A-cm}^{-2}$	Radiation time, min	Area resistivity, $\text{ohm-cm}^2$	Resistivity, $\text{ohm-cm}$
100	0	0	0.16	16
110	$10^{-7}$	5	.10	9.1
110	$10^{-7}$	15	.14	13
130	$10^{-7}$	30	.13	10

1. Report No. <b>NASA TP-1407</b>		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle <b>THREE METHODS FOR IN SITU CROSS-LINKING OF POLYVINYL ALCOHOL FILMS FOR APPLICATION AS ION-CONDUCTING MEMBRANES IN POTASSIUM HYDROXIDE ELECTROLYTE</b>				5. Report Date April 1979	
				6. Performing Organization Code	
7. Author(s) <b>Warren H. Philipp and Li-Chen Hsu</b>				8. Performing Organization Report No. <b>E-9778</b>	
9. Performing Organization Name and Address <b>National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135</b>				10. Work Unit No. <b>506-16</b>	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>				13. Type of Report and Period Covered <b>Technical Paper</b>	
				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract  <p>Three methods of in situ cross-linking polyvinyl alcohol films are presented. They are: (1) acetalization with a dialdehyde such as glutaraldehyde, (2) acetalization with aldehyde groups formed by selective oxidative cleaving of the few percent of 1,2 diol units present in polyvinyl alcohol, and (3) cross-linking by hydrogen abstraction by reaction with hydrogen atoms and hydroxyl radicals from irradiated water. For the third method, improvement in film conductivity in KOH solution at the expense of mechanical strength is obtained by the presence of polyacrylic acid in the polyvinyl alcohol films. Resistivities in 45 percent KOH are given for in situ cross-linked films prepared by each of the three methods.</p>					
17. Key Words (Suggested by Author(s)) <b>Battery separators Electrochemistry Polymer chemistry Membrane and film chemistry</b>			18. Distribution Statement <b>Unclassified - unlimited STAR Category 23</b>		
19. Security Classif. (of this report) <b>Unclassified</b>		20. Security Classif. (of this page) <b>Unclassified</b>		21. No. of Pages <b>17</b>	
				22. Price* <b>A02</b>	